The Effect of Hydrogen on the Discharge of Negative Electricity from Hot Platinum.

By Professor H. A. WILSON, F.R.S., King's College, London.

(Received January 23,—Read February 13, 1908.)

(Abstract.)

The effect of hydrogen on the discharge of negative electricity from hot platinum was examined by the writer in 1903;* it was found to produce a very large increase in the current. The experiments were all done with nearly new platinum wires which had not been heated in the gas for any great length of time, because it was known that long-continued heating causes the wire to disintegrate. The present paper contains an account of a series of experiments in which wires were heated for long periods in hydrogen, so that any changes in the effect of the hydrogen could be observed. It appears that continued heating in hydrogen alters the character of the effects observed so that the behaviour of an old wire may be very different from that of a new one.

The following gives a short abstract of each section of the paper:—

1. Assuming that $x = \mathrm{B}p^n$, where x denotes the current per square centimetre of platinum at constant temperature, p is the pressure of the hydrogen, and B and n are quantities depending only on the temperature, and also that $x = \mathrm{A}\theta^{\frac{1}{2}}e^{-\mathrm{Q}/2\theta}$, where θ denotes the absolute temperature and A and Q depend only on the pressure; it is proved that: (1) $n = \alpha\theta^{-1} - c$, where α and c are constants; (2) $\mathrm{Q} = \mathrm{P} - 2\alpha \log p$; and (3) $\mathrm{A} = \mathrm{K}p^{-c}$. These equations are shown to agree with the observations.

Eliminating p from (2) and (3) gives $\mathrm{A} = \mathrm{K}e^{(\mathrm{Q}-\mathrm{P})c/2\alpha}$. It is shown that all the values of A and Q for new wires satisfy this relation, including those for wires in air. The equation (3) is therefore modified to $\mathrm{A} = \mathrm{A}_0/(1+ap^c)$, where A_0, equal to $\mathrm{K}/(1+a)$, is the value of A in air or when $p=0$. This equation represents all the values of A. With (4) this gives

$$\mathrm{Q} = \mathrm{Q}_0 - 2\alpha c^{-1} \log(1+ap^c).$$

The equation $x = \mathrm{A}\theta^{\frac{1}{2}}e^{-\mathrm{Q}/2\theta}$ may now be written

$$x = \mathrm{A}_0(1+ap^c)^{(\alpha/\theta c-1)}\,\theta^{\frac{1}{2}}e^{-\mathrm{Q}_0/2\theta}.$$

If $\mathrm{R} = \mathrm{Q}_0 + 2(\theta - \alpha c^{-1}) \log(1+ap^c)$, then $x = \mathrm{A}_0\theta^{\frac{1}{2}}e^{-\mathrm{R}/2\theta}$, so that the effect of hydrogen can be represented by supposing that it changes Q without altering A.

* 'Phil. Trans.,' A, vol. 202, 1903, p. 352.

If $D = A_0(1+ap^c)^{(a/\theta c-1)}$, then $x = D\theta^{\frac{1}{2}}e^{-Q_0/2\theta}$, so that the effect of hydrogen can be represented by supposing that it changes A without altering Q.

These formulæ are shown to be in agreement with observations by different observers over a very wide range of temperature and pressure.

Assuming that the effect of the hydrogen is due to its presence in the surface layer of the platinum, the conclusion is drawn that the hydrogen in new wires is dissolved in the platinum. The agreement between the formulæ obtained and the observations shows that the equation $x = Bp^n$ which was assumed at the start is correct.

2. It is shown that the leak from a wire which has been heated in hydrogen at a high pressure for some time is nearly independent of the pressure at constant temperature between 0 and 200 mm. of mercury. The conclusion is drawn that the wire contains hydrogen in a state of stable chemical combination, and some experiments are described which seem to support this view.

3. The variation of the leak with the temperature, from a wire giving a leak independent of the pressure, is measured, and Q is found to be 135,000 and A to be $1{\cdot}67 \times 10^{10}$. These values do not satisfy the relation $A = Ke^{(Q-P)c/2a}$ which agrees with all the values of A and Q for new wires. On heating the wire in air, and then again in hydrogen at a small pressure, it is found to give the same leak as a new wire in hydrogen; but the leak takes a longer time than before to get to its final value after the pressure has been changed. The conclusion is drawn that heating in hydrogen at a high pressure produces a permanent change in the state of the platinum, which is not removed by heating in air, and which causes the hydrogen to dissolve more slowly in the platinum, but does not affect the final value of the leak. The leak in air is about the same at high temperatures as with a new wire.

4. It is shown that a wire which has been heated in hydrogen at a high pressure, and then in air, on heating in hydrogen at 1600° C. gives the same leak as in air. But at lower temperatures the leak after a time rises to the usual value in hydrogen, and is then large at 1600° C. also. The conclusion is drawn that the wire does not absorb hydrogen above 1600° C. If the temperature is raised when the leak has only partially recovered from its initial very small value, then it falls on raising the temperature and rises again on lowering it.

5. It is shown that the resistance of the wire is slightly increased when it absorbs hydrogen. A wire giving a large leak independent of the pressure was heated for some hours in a good vacuum, and then on heating in air the resistance fell slightly. The conclusion is drawn that the wire still contained

hydrogen. Reasons are given for believing that the stable compound only exists in the surface layer of the platinum.

6. In this section it is shown that the recovery of the leak described in Section 4 can be accelerated by passing an ordinary discharge through the gas from the wire to a neighbouring electrode.

7. The negative leak in hydrogen is compared with the positive leak in oxygen, and it is shown that there is a close analogy between them.

The conclusion is drawn that the negative leak is produced by hydrogen in the same way that the positive leak is produced by oxygen.

In the absence of hydrogen there is, however, a small negative leak due to the platinum alone.

8. In this section it is shown that if the true value of A in the formula $x = A\theta^{\frac{1}{2}}e^{-Q/2\theta}$ is denoted by D, and if D is supposed to be unaffected by the hydrogen, then the true value of Q is given by the equation

$$R = Q + 2\theta \log (D/A).$$

It is shown that the variation of the negative leak from lime with the temperature, as measured by Dr. Horton, is not really inconsistent with the view that D is proportional to the number of free electrons per cubic centimetre of lime.

9. This section contains a theory of the variation of R with the temperature. It is assumed that there is an electrical double layer at the surface of the platinum, and that the electric force in this layer is increased by the presence of electrons in it between the two layers. The increase due to this cause is shown to be greater at higher temperatures. It is shown that

$$R = Nw/J + 4\pi N\rho_0 e^3 t^3 \beta_0{}^2\theta^2/Jw^2,$$

where w is $4\pi\sigma t$, σ is charge per unit area in the layers, and t is distance between the layers. This gives

$$Q^2 \log (D/A) = 4\pi N^3 e^3 \rho_0 t^2 \beta_0{}^2 \theta / J^3.$$

It is found that a value for D can be obtained which makes $Q^2 \log D/A$ nearly constant. This is explained by supposing that the hydrogen atoms in the platinum are positively charged, and act by neutralising some of the negative charge in the double layer without altering t.

Adopting this value of D as the true value, t is found to be $2{\cdot}6 \times 10^{-8}$ cm., which agrees with the thickness of the double layer on platinum polarised by hydrogen in dilute sulphuric acid. The charge carried by the free electrons in 1 c.c. of the platinum is found to be $-2{\cdot}73 \times 10^{14}$ electrostatic units, which shows that there are eight free electrons to each atom of platinum.

This agrees with the fact that platinum is an octovalent element. The values found for R are the following :—

Gas.	Pressure.	R.
	mm.	
Air	—	$145{,}000 + 9 \cdot 68\,\theta$
H_2	0·0013	$110{,}000 + 19 \cdot 15\,\theta$
H_2	0·112	$90{,}000 + 25 \cdot 14\,\theta$
H_2	133	$56{,}000 + 36 \cdot 18\,\theta$

The value of D adopted is $1 \cdot 44 \times 10^{10}$, but this may be in error by a factor of 10 or more.

Conclusion.

The view taken in this paper is that the effect of the hydrogen on the leak is due to its presence in the surface layer of the platinum. To explain this it is supposed that the hydrogen atoms in the layer are positively charged, so that they diminish the charge per unit area in the electrical double layer covering the surface of the platinum. The hydrogen appears to dissolve in the platinum at first, but at high pressures in time forms a stable combination with the platinum, having a very small dissociation pressure. Before this compound has been formed, the leak is proportional to a power of the pressure of the hydrogen.